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COMPLETE SPECIFICATION

Galactomannan Gum Solutions and Process

We, STEIN, HALL & CO. INC., a corporation of the State of New York, United States of America, having an office and place of business at 285, Madison Avenue, New York, New York, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a process for retarding the rate of degradation of colloidal aqueous solutions of galactomannan materials at elevated temperatures. In addition, the invention relates to compositions for use in preparing colloidal aqueous solutions of galactomannans, which solutions have a reduced rate of degradation.

Colloidal aqueous solutions of galactomannan materials are used for a variety of purposes under temperature conditions which, within a very short time, cause a breakdown of the material and a consequent decrease or complete loss of viscosity or other desirable characteristic of the solution. In many instances, the primary reason for employing the galactomannan is to impart and maintain a desirable viscosity. In other instances, the material is employed as a precipitant or flocculant, or is merely maintained in the form of a hot solution or suspension during use. In any event, the instability of these materials in the presence of water under conditions of relatively high temperatures is a severe disadvantage.

An example of this problem is found where guar gum is used in steam boiler water treatment. In this instance, the guar gum is placed in the water line feeding the steam boiler, and is slowly dispensed into the water flowing into the boiler. The guar gum tends to prevent encrustation of the boiler with mineral deposits, or if the minerals are deposited, to facilitate the removal thereof. If the guar gum solution is held at a high temperature over a period of time, however, the gum degrades and much of the benefit obtained by employing

the gum is lost.

According to the invention, a composition for use in preparing a colloidal aqueous solution of a galactomannan material of improved stability at elevated temperatures and at a pH above about 5.5, comprises a galactomannan, and a salt, selected from water-soluble metal sulphites, thiosulphates and arsenites, which is effective in retarding degradation of the galactomannan material in the presence of water at elevated temperatures.

The invention also includes a process of retarding the degradation of a galactomannan material in the presence of water at an elevated temperature and at a pH above about 5.5 which comprises the addition to a colloidal aqueous solution of said material, a salt, selected from water-soluble metal sulphites, thiosulphates and arsenites, which is effective in retarding degradation of the carbohydrate material in the presence of water at elevated temperatures.

Examples of suitable salts include sodium sulphite, zinc sulphite, sodium thiosulphate, and sodium arsenite. In addition, it has been found necessary, in many instances, that sodium chloride be present in order to render the salt from the stated group effective, or to increase the effectiveness thereof.

Certain other inorganic salts have also been found to provide an additive effect when employed with the salts listed above, although when employed alone they are found to have little or no effect. These include disodium phosphate, trisodium phosphate and sodium tripolyphosphate.

The galactomannan materials to which this invention relates are polysaccharides, generally termed hemicelluloses, and are long chain polymers of galactose and mannose units. While their exact composition is not known, they have been found to yield these two sugars on hydrolysis. They are gum-like materials, generally found in plant seeds. Examples of the galactomannans are guar gum, obtained from *Cyamopsis tetragonolobus* (a legume); locust bean gum, obtained from *Ceratonia*

siliqua; and tara gum, obtained from *Cesalpinia spinosa*.

The pH of the solution is a critical factor if the desired viscosity or other characteristics of the galactomannan in colloidal aqueous solution is to be obtained over a period of time under high temperature conditions. Generally speaking, at a pH below about 5.5, the solutions are unstable at high temperatures, regardless of whether the salts or combination of salts which may be employed according to this invention are utilized. Above a pH of about 5.5, the galactomannans are favorably influenced by the presence of the salt additives. It is preferred, in the case of guar gum, that a pH of from about 8—10 be utilized.

Not all of the salts of the group listed above function to improve the stability of all of the galactomannan materials to the desired extent. In some instances, a given salt will be more effective than the others. For example, in the case of tara gum, sodium sulphite is extremely effective in retarding degradation at elevated temperatures. On the other hand, sodium thiosulphate has only a slight effect. It should be noted, however, that sodium thiosulphate in combination with a small amount of disodium phosphate is very effective. On the other hand, sodium sulphite has practically no effect on guar gum stability, while sodium thiosulphate slows the rate of degradation of the guar gum considerably.

Another important factor to be considered according to this invention is the presence of sodium chloride, which, when used with one or more of the other salts listed, in most cases effects marked improvement over the use of the other salt alone. In the case of sodium and zinc sulphite, when used with guar gum for example, the presence of sodium chloride is nearly essential in providing a substantial stabilizing effect. As the sodium chloride concentration is increased, the rate of degradation of the material is decreased.

When using sodium thiosulphate to stabilize guar gum in colloidal aqueous solutions, the presence of sodium chloride is not essential to provide a significant improvement in stability. However, if sodium chloride is used, a decreased rate of degradation is noted, the stability increasing with the sodium chloride concentration.

In still further instances, the presence of sodium chloride is actually harmful. This is true with tara gum where the addition of sodium chloride to a solution of the gum containing sodium sulphite or sodium thiosulphate reduces the stability of the solution.

Although the majority of the salts described above are generally considered to be reducing agents, it is not believed that the results obtained according to this invention are due to this property. Several other inorganic reducing agents including an oxalate, a nitrite, ferrous sulphate, stannous chloride, hydro-

sulphite, and disulphite, have been tested and found to be ineffective in reducing the rate of degradation of galactomannans in colloidal aqueous solutions.

Regarding the concentration of salts which may be employed according to this invention, it has been found that 5% sodium thiosulphate, 2.5% sodium sulphite, and 10% zinc sulphite are the minimum concentrations which will provide a desired stability. Salt levels substantially lower than these values may prove to be of some benefit, but are generally less than satisfactory. The upper range of concentrations is limited by possible adverse side effects caused by a high concentration of electrolyte in the solution and by the expense of the additive.

It has also been found that certain other compositions, when present in a small amount lengthen the life of the solution by, in some instances, a few days. For example, disodium phosphate, trisodium phosphate, and sodium tripolyphosphate slightly increase the initial viscosity of the solution and also the stability without obtaining too high a viscosity. These effects are shown in the examples below.

The following specific examples are set forth to more clearly define the processes and products of this invention.

EXAMPLE 1.

Guar gum is a common flocculating agent for use in the treatment of boiler water. When used in this capacity, the boiler water is maintained at a relatively high temperature for long periods of time. It is desirable that the rate of degradation of the guar gum under these conditions be reduced. The tables 1 to 5 below show the improvement in viscosity stability of guar gum solutions held at elevated temperatures for the indicated periods of time. A high quality edible grade of guar gum was employed and the solutions were prepared at a 1% gum concentration. Unless otherwise specified all percentage concentrations in the tables are based on the weight of the guar gum in solution with the exception of the sodium chloride, which is based on the weight of the total solution. All solutions were held at the indicated temperature in sealed jars for the indicated periods of time. When tested, the jars were cooled, opened and the viscosity measured by a Brookfield viscosimeter at 25° C. and at 20 r.p.m. Where pH adjustment was required, acid or alkali was added to the solution before any appreciable swelling of the guar gum had taken place.

It should also be noted that in the tables 1—5 and 7, the "0" time determinations were taken after the gum had been allowed to dissolve in cold water for two hours. In Table 6, the "0" time determinations were obtained on solutions which had been heated at about 100° C. for a time sufficient to dissolve the locust bean gum, and then cooled for two hours prior to determining the viscosity.

TABLE 1

This table shows the effect of pH on the guar gum solution in the presence of sodium chloride and sodium sulphite after holding the solution at 80° C. for the periods of time indicated.

	(1)		(2)		(3)		(4)		(5)		(6)		(7)
	Visc	pH	Visc	pH	Visc	pH	Visc	pH	Visc	pH	Visc	pH	
Sodium Chloride %	10	3.4	10	5.0	10	6.3	10	8.4	10	9.0	10	10	—
Sodium Sulphite %	10	—	10	—	10	—	10	—	10	—	10	—	—
Initial pH	3.5	—	5	—	6.5	—	8.5	—	9.5	—	8.5	—	6.5
Time (days)	Visc	pH	Visc	pH	Visc	pH	Visc	pH	Visc	pH	Visc	pH	
0	—	—	—	—	2300	—	—	—	—	—	2100	—	2300
1	10	3.4	10	5.0	2500	6.3	2980	8.4	2450	9.0	1180	7.0	1240
2	—	—	—	—	2500	6.5	2810	8.6	1900	8.7	800	7.0	240
5	—	—	—	—	2020	6.8	2400	9.1	1640	9.3	—	—	—
9	—	—	—	—	1050	7.9	2000	9.1	1230	9.2	—	—	—
13	—	—	—	—	600	7.6	1320	9.2	840	9.4	—	—	—
14	—	—	—	—	—	—	1240	9.1	—	—	—	—	—
16	—	—	—	—	—	—	1000	9.1	—	—	—	—	—

It can be seen from Table 1 that in the presence of sodium chloride and sodium sulphite, degradation of the guar gum solution is substantially retarded within a pH range of about 6.5 to about 9.5 with a pH of about 8.5 being preferred.

TABLE 2

This table illustrates the effectiveness of sodium sulphite, both alone and in combination with sodium chloride and disodium phosphate in retarding the rate of degradation of a 1% guar gum solution held at 80° C. for the indicated periods of time.

[illegible]

TABLE 3

This table illustrates the effectiveness of sodium thiosulphate, both alone at various levels and in combination with sodium chloride and other additives in stabilizing a 1% guar gum solution at 80° C.

	(1)		(2)		(3)		(4)		(5)		(6)		(7)	
	Visc	pH	Visc	pH	Visc	pH	Visc	pH	Visc	pH	Visc	pH	Visc	pH
Sodium Chloride %	—	—	10	—	(at pH 10)	10	10	10	10	10	10	10	10	10
Sodium Thiosulphate %	10	10	10	10	10	10	5	5	5	5	5	5	5	5
Sodium Tripolyphosphate %	—	—	—	—	—	—	—	—	5	5	—	—	—	—
Trisodium phosphate %	—	—	—	—	—	—	—	—	—	—	5	5	—	—
Disodium phosphate %	—	—	—	—	—	—	—	—	—	—	—	—	5	5
Time (days)	Visc	pH	Visc	pH	Visc	pH	Visc	pH	Visc	pH	Visc	pH	Visc	pH
0	—	—	—	—	2140	—	—	—	—	—	—	—	—	—
1	3510	6.8	3050	6.7	3120	7.1	3050	6.5	3160	6.6	3160	7.1	3200	6.7
2	3080	7.3	2630	8.2	—	—	2740	6.8	2930	6.5	2960	8.5	2960	6.7
5	—	—	—	—	2740	8.9	1940	8.8	—	—	—	—	1740	7.5
6	1440	6.9	—	—	2600	9.0	—	—	1540	7.7	2480	8.9	1560	7.8
7	1040	6.7	2050	8.7	2530	9.0	—	—	1400	7.6	2550	8.9	1400	8.1
9	—	—	1740	8.6	—	—	—	—	1140	7.5	2340	8.5	860	8.0
10	—	—	1580	8.3	—	—	—	—	940	7.2	2300	8.3	—	—
11	—	—	1480	8.1	2200	8.9	—	—	—	—	—	—	—	—
14	—	—	1270	7.6	1740	8.8	—	—	—	—	1900	8.3	—	—
16	—	—	1090	8.2	—	—	—	—	—	—	1280	8.0	—	—
17	—	—	860	7.8	—	—	—	—	—	—	1180	8.2	—	—
19	—	—	—	—	1300	8.6	—	—	—	—	—	—	—	—
20	—	—	—	—	1130	8.5	—	—	—	—	1010	8.2	—	—

TABLE 4

This table shows the effectiveness of sodium arsenite and zinc sulphite in retarding the degradation of a 1% guar gum solution held at 80° C. for the periods of time indicated.

	(1)		(2)		(3)	
Sodium chloride %	—		10		10	
Sodium arsenite %	—		10		—	
Zinc sulphite %	—		—		10	
Initial pH	—		—		8.5	
Time (days)	Visc	pH	Visc	pH	Visc	pH
0	2400	—	—	—	2520	—
1	1240	6.2	2960	9.1	2760	7.5
2	240	5.7	—	—	—	—
4	—	—	—	—	2000	7.5
5	—	—	2750	9.0	1640	7.5
6	—	—	2680	9.0	1350	7.5
8	—	—	2450	9.0	650	7.2
11	—	—	2160	9.0	—	—
13	—	—	1860	9.0	—	—
15	—	—	1540	9.0	—	—
19	—	—	1000	8.8	—	—

TABLE 5

This table shows the effectiveness of sodium sulphite in retarding the degradation of 1% guar gum in aqueous solution held at 121° C. for the periods of time indicated.

Sodium Chloride %	10	30	10	10	30	
Trisodium Phosphate %	—	—	—	10	25	
Disodium phosphate %	—	—	100	—	—	
Sodium Sulphite %	10	10	10	10	10	
Initial pH	—	9.5	8.2	9.7	9.3	
Time (days)	Visc	pH	Visc	pH	Visc	pH
0	—	—	1700	—	2300	—
1	5	5.8	1350	6.8	2450	7.9
2	—	—	100	—	1950	7.7
3	—	—	—	—	1350	7.7
4	—	—	—	—	950	7.7
6	—	—	—	—	800	7.3
7	—	—	—	—	160	7.6
					2080	8.3

It will be noted from the above that the use of sodium sulphate in combination with sodium chloride is not sufficient to impart a substantial stability to the solution at this temperature. The addition of disodium phos-

phate, or trisodium phosphate, results in considerable improvement.
EXAMPLE 2.
The following series of tables illustrates the effectiveness of the various indicated salts in

reducing the rate of degradation of locust bean gum and tara gum solutions in the presence of water at elevated temperatures.

TABLE 6

Table 6 shows the stabilizing effect of sodium sulphate and sodium thiosulphate in combination with sodium chloride and trisodium phosphate in an aqueous solution of locust bean gum held at 100° C. for the indicated periods of time.

	(1)	(2)	(3)	(4)	(5)	(6)	(7)
Locust bean gum, (high grade) %	1	1	1	1	1	1	1
Sodium Sulphate %	—	10	10	—	—	—	—
Sodium Thiosulphate %	—	—	—	10	10	10	10
Sodium chloride %	—	—	10	—	—	10	10
Trisodium phosphate %	—	0.25	—	—	0.25	—	0.25
Time (days)	Visc	pH	Visc	pH	Visc	pH	Visc
0	2500	—	—	—	—	—	—
2	310	—	1860	—	260	—	1180
3	136	6.3	1820	1070	430	—	1130
6	80	8.5	1390	980	400	9.8	890
9	—	—	1320	950	580	9.1	780
	—	—	800	9.4	—	9.2	8.6

The concentrations of the locust bean gum, sodium chloride and trisodium phosphate are based on the total solution. The concentrations of all other materials are based on the locust bean gum. Viscosities were determined with a Brookfield viscosimeter at 25° C. and at 20 r.p.m.

TABLE 7

This table shows the benefits of using sodium sulphite, sodium thiosulphite, sodium chloride and trisodium phosphate with a solution of technical grade of tara gum held at 100° C. for the times indicated.

	(1)		(2)		(3)		(4)		(5)		(6)		(7)		(8)	
	Visc	pH	Visc	pH	Visc	pH	Visc	pH	Visc	pH	Visc	pH	Visc	pH	Visc	pH
Tara gum % (technical)	3		3		3		3		3		3		3		3	
Sodium sulphite %	—		10		10		10		10		—		—		—	
Sodium thiosulphate %	—		—		—		—		—		10		10		10	
Sodium chloride %	—		—		—		10		10		—		—		10	
Trisodium phosphate %	—		—		0.25		—		0.25		—		0.25		—	
Time (days)	Visc	pH	Visc	pH	Visc	pH	Visc	pH	Visc	pH	Visc	pH	Visc	pH	Visc	pH
0	6700	—	—	—	6800	—	—	—	—	—	—	—	—	—	—	—
1	—	—	10000	—	10800	—	—	—	—	—	—	—	—	—	8480	—
2	148	—	9060	—	11750	—	6570	—	10000	—	172	—	11360	—	7200	—
3	46	4.7	7080	—	7400	7.7	5700	—	1910	—	46	—	7750	—	1370	—
6	—	—	3280	6.5	3980	7.8	1760	6.2	1720	7.5	24	5.2	5200	6.4	610	6.0
9	—	—	—	—	—	—	580	7.0	730	6.1	—	—	300	6.6	—	—

The concentrations of the tara gum, sodium chloride and trisodium phosphate are based on the total solution. The concentrations of all other materials are based on the tara gum. Viscosities were determined with a Brookfield viscosimeter at 25° C. and at 20 r.p.m.

It is understood that the foregoing examples are illustrative only and that modifications will occur to those skilled in the art. Therefore, the invention is not to be limited thereto but is to be defined by the appended claims.

WHAT WE CLAIM IS:—

1. A composition for use in preparing a colloidal aqueous solution of improved stability at elevated temperatures and at a pH above about 5.5, comprising a galactomannan, a salt selected from water-soluble metal sulphites, thiosulphates and arsenites which is effective in retarding degradation of the galactomannan material in the presence of water at elevated temperatures.

2. A composition as claimed in claim 1, which also contains sodium chloride.

3. A composition as claimed in claim 1 or claim 2 in which the galactomannan is guar gum.

4. The composition of claim 1, 2 or 3, wherein the salt is zinc sulphite.

5. The composition of claim 1, 2 or 3,

wherein the salt is sodium sulphite.

6. The composition of claim 1, 2 or 3, wherein the salt is sodium arsenite.

7. The composition of claim 1, 2 or 3, wherein the salt is sodium thiosulphate.

8. The process of retarding the degradation of a galactomannan material in the presence of water at elevated temperatures and at a pH above about 5.5 comprising the addition to a colloidal aqueous solution of said material, a salt selected from water-soluble metal sulphites, thiosulphates and arsenites, which is effective in retarding degradation of the carbohydrate material in the presence of water at elevated temperatures.

9. A composition for use in preparing a colloidal aqueous suspension of galactomannan materials substantially as described.

10. A colloidal aqueous solution of galactomannan materials substantially as described.

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